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Harmful Algal Bloom (HAB) and Cyanotoxin: Treatment and Management for Public Water Systems

CITY OF MARION WATER PLANT

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Algae can cause many different drinking water treatment issues. The most common issues affect water taste and odor, clog intake screens and filters, disrupt the settling process, increase chemical and chlorine demand and elevate disinfection by-products. Monitoring for and treating algal toxins are now added to that list.

Currently the USEPA does not regulate algal toxins. However, three (3) algal toxins are on the Candidate Contaminant List 3 (CCL3): anatoxin-a; microcystin-LR; and cylindrospermopsin. EPA has also indicated that these 3 toxins will be included in the Unregulated Contaminant Monitoring Rule 4, currently scheduled for a 2016 release. In addition, EPA is presently developing a Health Advisory document to identify safe levels for drinking water use.

Most public water systems and health agencies rely on the World Health Organization's (WHO) guideline of 1.0 ppb (parts per billion, or micrograms/liter, or µg/L) for microcystin LR. As there is no federal regulation or established limits, states have set their own: Ohio, Oregon and Oklahoma have a limit of 1 ppb for microcystin-LR, while Florida's is at 10 ppb. Other countries have set standards as well; for example, Australia has proposed a limit of 1.3 ppb for total microcystins and Canada has set the value at 1.5 ppb.

Once cyanobacteria (also known as harmful algae) and/or their cyanotoxins are detected in the water supplying the drinking water system, the plant operators can act to remove or inactivate the algae and their toxins in a number of ways. Treatment options vary according to the type of algae or toxins present. Thus, drinking water operators need to know the growth patterns and species of cyanobacteria in the bloom, the properties of the cyanotoxins (i.e., intracellular or extracellular) and the most effective treatment process. Applying the wrong treatment or applying treatment at the wrong time could damage cells and result in the release rather than removal of cyanotoxins.

Source water strategies:

Environmental factors that affect the formation and persistence of cyanobacteria blooms include light intensity and total sunlight duration, nutrient availability (especially phosphorus), water temperature, pH, an increase in precipitation events, water flow (whether water is calm or fast-flowing), and water column stability. Although bloom conditions in much of the US are more favorable during the late summer, the interrelationship of the factors above can result in large seasonal and year-to-year fluctuations in the cyanobacteria levels. Some toxin-producing strains can occur early in the summer season, while others are generally only found during late summer, and some cyanobacteria persist year-round. Both reservoirs and rivers can be affected.

Water treatment operators should implement a raw water monitoring program that includes

parameters such as pH, dissolved oxygen, water temperature, color, odor, water clarity (Secchi disk) and turbidity. Other parameters that could be analyzed at the treatment plant include chlorophyll a, nitrogen, phosphorus and algal cell counts. Monitoring should occur at the surface and at various depths, particularly at depths from which water is typically drawn for treatment. Developing a means to compare historical and current results can help with choosing the appropriate control option.

Stay aware of weather conditions and patterns within the watershed to help prepare for bloom conditions.

To avoid the release of cyanotoxins into the water, operators can use source water strategies to deal with cyanobacteria blooms. These include:

- Using an unaffected source water;
- Using an alternate intake level;
- Providing in-source aeration; and
- Discontinue use of the affected raw water and purchase water from another PWS.

Algaecides, such as copper sulfate products, can control the growth of algae under certain conditions. Source treatment should be applied cautiously at the early stages of a bloom when the potential for toxin release is not likely or is low. The lower level of toxins, if released into the water, can then be removed effectively during the treatment processes. Systems should not use algaecides to treat excessive blooms unless the source is not immediately needed and appropriate testing can be conducted to ensure toxins are not present. To keep the algae under control for extended periods of time, the algaecide applications should be performed at specific intervals based upon the pesticide label.

NOTE: Copper sulfate and other algaecides may be considered "pesticides" and require a state pesticide application license and a NPDES permit. It is also important to read the product label to fully understand both the environmental impact and practical problems with its use.

A watershed and/or source water protection program can help reduce the nutrient load in the source water. An effective program can help identify specific environmental characteristics of the watershed and actions necessary to reduce or eliminate potential contaminants.

Drinking Water Treatment Strategies:

Pretreatment

Pretreatment oxidation at the intake is often used to reduce taste and odor compounds, zebra mussels and other contaminants; however Pretreatment oxidation can break open (called "lysing") the algal cells and potentially release toxins:

- Copper sulfate and ozone at the intake removes the algal bloom, but also have the risk of

lysing the algal cells.

- Chlorination, in addition to lysing the cells, could also produce disinfection by-products. Literature and studies support discontinuing pre-chlorination during the blooms.
- Potassium or sodium permanganate can be used to control manganese and iron with less of an effect on *Microcystis* and *Anabaena*. Permanganate may also be effective in oxidizing anatoxins and microcystins. It is recommended that powdered activated carbon (PAC) be added to remove any toxins that may have been released and not inactivated.

Coagulation/flocculation/sedimentation

The standard drinking water treatment processes (coagulation, flocculation, sedimentation and filtration), have various levels of effectiveness in removing whole algal cells and intracellular cyanotoxins. Coagulation/flocculation with dissolved air flotation (DAF) and with sludge blanket clarifiers is more effective than with conventional processes.

Treatment processes should be optimized to maximize removal of total organic carbon, turbidity and color. This approach may involve adjusting loading rates, chemical dosages and detention times. Studies show that coagulation above pH of 6.3 will prevent the lysing of cells. Alternately, other studies have shown coagulation with common coagulants (alum, ferric, polyaluminum chloride) to be ineffective for toxin removal. Be aware that turbidity alone has not shown to be a reliable indicator of the presence of cyanobacteria, cell counts, or the presence of cyanotoxins. In addition, treatment optimization may lead to increased production costs.

Filtration

When a bloom occurs and cells are carried through to the filters, filtration rates should be decreased and filters backwashed more frequently to reduce the risk of toxins being release into the water. If necessary, use a filter aid.

Slow sand filtration has shown, in some studies, to be more effective in removing algal cells than rapid sand filtration.

NOTE: If the plant recycles spent filter backwash, this practice should be discontinued to avoid the recycling of algal cells and/or toxins back into the plant.

Microfiltration and ultra-filtration are highly effective at removing intact cyanobacteria cells as well as intracellular and particulate toxins. Nano-filtration and reverse osmosis are effective in removing cylindrospermopsin and microcystin. However, site-specific tests are recommended to track removal efficiency as this depends on the membrane pore size distribution and water quality.

Adsorption (powdered and granular activated carbon)

Extracellular toxins can be removed using activated carbon (both powdered and granular), membrane filtration and chemical inactivation (disinfectants, oxidants and UV). However, this is achieved at very high dosages of PAC (powdered activated carbon (20 mg/L and higher) and extended contact times. Granular activated carbon (GAC) filters may require increased regeneration frequencies.

Both PAC and GAC can be effective in absorbing microcystin and cylindrospermopsin, although microcystin variants may have different adsorption efficiencies. The performance of activated carbon depends on the concentration of the toxin and the dose and origin of the activated carbon (wood-based carbons have been demonstrated to be more effective than other carbon sources). Jar tests are recommended to test the effectiveness of various PAC types.

Repeated treatment may be needed to remove the toxins completely.

Oxidation and Disinfection

UV treatment, although effective in destroying microcystin, anatoxin-a, and cylindrospermopsin cells, requires higher doses than are practicable, reducing it's viability as a treatment option. UV has been used along with a catalyst (titanium dioxide) to oxidize the toxins. However, the effectiveness of this process is largely dependent on the organic content of the water.

Oxidants like chlorine, ozone and permanganate can effectively inactivate microcystin.

- Various cyanotoxins react differently to chlorin; with removal effectiveness commonly being pH-dependent. For example, chlorine has been shown to be ineffective against anatoxin-a. However, when the pH is less than 8, chlorine can effectively inactivate microcystin and cylindrospermopsin.
- Ozone can effectively oxidize of microcystins, anatoxin-a and cylindrospermopsin, but it is also pH-dependent and may be affected by the presence of organic matter. For example, the effectiveness of ozone is pH-independent for microcystin but is pH-dependent for of anatoxin-a (pH 7 to 10) and for cylindrospermopsin (pH 4 to10).
- Permanganate is effective in oxidizing microcystin and anatoxin-a (from pH 6 to 8), but is not very reactive with cylindrospermopsin.
- Chloramines and chlorine dioxide are not effective treatments for microcystin, anatoxin-a and cylindrospermopsin.

Chlorine C-T information for inactivating microcystin-LR can be found in Table 1.

The formation of disinfection by-products is another potential problem with the use of oxidants or disinfectants in pre-treatment. Oxidants and disinfectants should be used in pre-treatment after careful consideration of the raw water quality. Results from studies on the chlorination of cell-bound toxins and resulting disinfection by-products formation are contradictory. However, the majority of the findings suggest that pre-chlorination should ideally be avoided during blooms.

Residuals (Sludge) Handling

Water treatment residuals, both liquid and solid, can contain whole and lysed algal cells as well as toxins. As noted above, spent filter backwash recycling should be discontinued during periods of algal blooms. Solids removed from sedimentation basins and filters can contain viable cyanobacteria for up to 3 weeks; toxin release could occur in as little as 1 day.

Table 2 summarizes the effectiveness of different types of water treatment to remove intact cyanobacteria cells and that are effective in removing extracellular dissolved toxins of several of the most important cyanobacteria. Drinking water operators are encouraged to monitor the treated water to guarantee the removal of cyanotoxins.

Develop a Contingency Plan

Drinking water systems should develop a contingency plan for cyanobacteria/harmful algal blooms. Most algal blooms are not toxic and the plan should address how to determine the risk associated with each event. Elements of such a plan should include a sampling component as well as a response strategy should cell counts or toxin levels be above a recommended threshold.

The plan can include:

- Sampling procedures, including sites, frequency, sampling equipment;
- Parameters to be monitored such as cyanobacteria levels, toxins, other parameters (such as chlorophyll a);
- Analytical capability for both biological assays and chemical instrumentation methods;
- Alternate finished water sources;
- Cleaning or flushing procedures; and
- Communication strategies with media, customers and regulatory agencies.

A spokesperson should be identified to handle public and media relations; others should tasked with maintaining communication with regulatory agencies and laboratories.

Where can I get more information?

For more information, please visit

- EPA's Cyanobacteria Harmful Algal Blooms web page at http://www.epa.gov/nandppolicy/links.html#hab
- Kentucky Division of Water HAB page at http://water.ky.gov/waterquality/pages/HABS.aspx

Table 1. Chlorine contact time values required for reducing microcystin LR concentration to 1 ug/L (from Oregon Drinking Water Services, "Best Management Practices for Harmful Algae Blooms for Drinking Water Providers")

Example: If you know the toxin level is 50 ppb and you want to reduce the level down to 1 ppb, with a temperature of 10° C and pH of 7, you will need a CT of 67.7. High pH water takes longer to degrade microcystin.

pH	Microcystin- LR Concentration	CT (mg/l x min)			
		10°C	**15°C**	**20°C**	**25°C**
6	50 ug/l	46.6	40.2	34.8	30.8
	10 ug/l	27.4	23.6	20.5	17.8
7	50 ug/l	67.7	58.4	50.6	44.0
	10 ug/l	39.8	34.4	29.8	25.9
8	50 ug/l	187.1	161.3	139.8	121.8
	10 ug/l	110.3	94.9	82.8	71.7
9	50 ug/l	617.2	526.0	458.6	399.1
	10 ug/l	363.3	309.3	269.6	234.9

- Westrick (2008) created a CT table based on research published by Acero et al., 2005.

Table 2. Cyanotoxin Treatment Processes and Relative Effectiveness (modified with additional information)

Treatment Process	Relative Effectiveness
Intracellular Cyanotoxins Removal (Intact Cells)	
Pretreatment oxidation	Avoid pre-oxidation because often lyses cyanobacteria cells releasing the cyanotoxin to the water
Coagulation/Sedimentation/ Filtration	Effective for the removal of intracellular toxins when cells accumulated in sludge are isolated from the plant and the sludge is not returned to the supply after sludge separation.
Membranes	Study data is scarce; it is assumed that membranes would be effective for removal of intracellular cyanotoxins. Microfiltration and ultra-filtration are effective when cells are not allowed to accumulate on membranes for long periods of time.
Flotation	Flotation processes, such as Dissolved Air Flotation (DAF), are effective for removal of intracellular cyanotoxins since many of the toxin-forming cyanobacteria are buoyant.
Oxidation processes	Avoid because often lyses cyanobacteria cells releasing the cyanotoxin to the water column.
Extracellular Cyanotoxins Removal	
Membranes	Depends on the material, membrane pore size distribution, and water quality. Nano-filtration and ultra-filtration are likely effective in removing extracellular microcystin. Reverse osmosis filtration would likely only be applicable for removal of some extracellular cyanotoxins like cylindrospermopsin. Cell lysis is highly likely. Further research is needed to characterize performance
Potassium Permanganate	Effective for oxidizing microcystins and anatoxins if intact cells are not present.. Further research is needed for cylindrospermopsin.
Ozone	Very effective for oxidizing extracellular microcystin, anatoxin-a and cylindrospermopsin.
Chloramines	Not effective
Chlorine dioxide	Not effective with doses used in drinking water treatment.
Chlorination	Effective for destroying microcystin LR at pH levels below 8 at a dosage of 0.5 mg/L for 30 minutes cylindrospermopsin can also be degraded using this treatment, ineffective for anatoxin-a.
UV Radiation	Effective of degrading microcystin and cylindrospermopsin but at very high dosages
Activated Carbon	PAC: Most types are generally effective for removal of microcystin, anatoxin-a and cylindrospermopsin, especially wood-based activated carbon. GAC: Effective for microcystin but less effective for anatoxin-a and cylindrospermopsin.

References Used:

EPA, "Cyanobacteria and Cyanotoxins: Information for Drinking Water Systems, July 2012

Conry, Tom and Sklenar, Karen, EPA Webinar, "How to Protect your Drinking Water from Harmful Algal Blooms", July 2014

Water Policy Report, www.InsideEPA.com, January 13, 2014

AWWA/Ohio EPA, "White Paper on Algal Toxin Treatment", June 2011

Oregon Drinking Water Services, "Best Management Practices for Harmful Algal Blooms (HABs) for Drinking Water Providers", January 2013

Water Research Foundation, Project Update, email to subscribers on August 4, 2014

Odell, Lee H., CH2M Hill, "The Impact of Water Treatment Processes on Algae and Toxins"